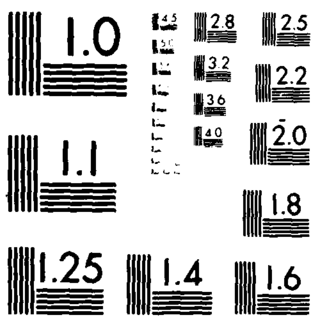
AD-A109 733   DAVID W TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CE--ETC   F/G 11/6
CREVICE CORROSION BEHAVIOR OF 45 MOLYBDENUM-CONTAINING STAINLES--ETC(U)
DEC 81   H P HACK
UNCLASSIFIED   DTNSRDC/SME-81/87   NL

1 of 1
AD
A109733

END
DATE
FILMED
82
DTIC



MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

1

(2) LEVEL

DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Maryland 20084

DTNSRDC/SME-81/87

AD A109733

CREVICE CORROSION BEHAVIOR OF 45 MOLYBDENUM-CONTAINING STAINLESS STEELS IN SEAWATER

by

Harvey P. Hack

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

SHIP MATERIALS ENGINEERING DEPARTMENT

RESEARCH AND DEVELOPMENT REPORT

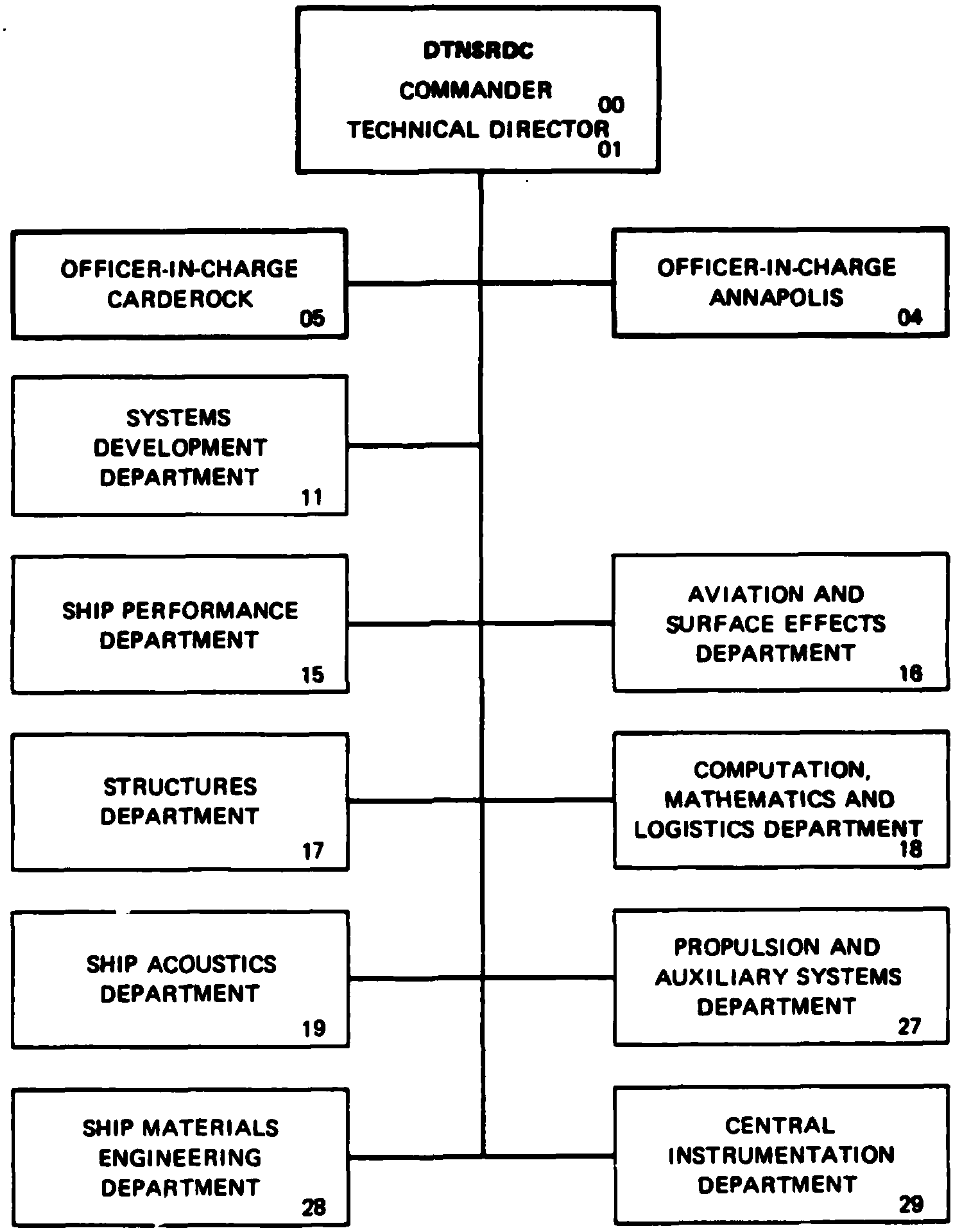
December 1981

DTNSRDC/SME-81/87

CREVICE CORROSION BEHAVIOR OF 45 MOLYBDENUM-CONTAINING STAINLESS STEELS IN SEAWATER

01 19 82 155

MAJOR DTNSRDC ORGANIZATIONAL COMPONENTS



UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DTNSRDC/SME-81/87	2. GOVT ACCESSION NO. AD-A109733	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CREVICE CORROSION BEHAVIOR OF 45 MOLYBDENUM-CONTAINING STAINLESS STEELS IN SEAWATER		5. TYPE OF REPORT & PERIOD COVERED Research and Development 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Harvey P. Hack		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS David W. Taylor Naval Ship R&D Center Annapolis, Maryland 21402		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element 62761N Task Area SF 61541-91 Work Unit 1-2813-610
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Sea Systems Command (SEA 05R15) Washington, D.C. 20362		12. REPORT DATE December 1981 13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Crevice Corrosion, Stainless Steels
Seawater Corrosion, Localized Corrosion

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thirty-six wrought and nine cast commercial molybdenum-containing stainless steels and nickel alloys were exposed to filtered natural seawater at 30°C for 30 days using multiple-crevice washers to create a crevice condition. The relative crevice corrosion behavior of these alloys in seawater is analyzed, and the effect of composition discussed.

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
°C	Degrees Celsius
l	Liter
mm	Millimeter
m/sec	Meters per second
N·m	Newton meter
No.	Number
UNS	Unified Numbering System of ASTM
wt %	Weight percent

ABSTRACT

Thirty-six wrought and nine cast commercial molybdenum-containing stainless steels and nickel alloys were exposed to filtered natural seawater at 30°C for 30 days using multiple-crevice washers to create a crevice condition. The relative crevice corrosion behavior of these alloys in seawater is analyzed, and the effect of composition discussed.

ADMINISTRATIVE INFORMATION

This project was funded under the Submarine Materials Technology Block Program sponsored by the Naval Sea Systems Command (SEA 05R15, Dr. H. H. Vanderveldt) and satisfies Milestone RD1.3/4. The work was performed under Program Element 62761N, Task Area SF61541-591, Work Unit 1-2813-610.

INTRODUCTION

Stainless steels are used primarily for their low cost and corrosion resistance, and have been successfully applied in a large variety of environments including acids, freshwater, and marine environments. Unfortunately, Type 316 which is generally considered one of the most corrosion-resistant of the common austenitic stainless steels, has not consistantly performed well under conditions of total immersion in seawater.[1,2*] This is due to the breakdown of the passive film on the stainless steel by the chloride ions in the seawater, which results in crevice corrosion under low flow conditions.

Usually, materials used for marine service include painted steels or copper-based materials such as copper-nickels or bronzes. If more corrosion resistance was required, nickel-base materials such as nickel-coppers and alloy 625, or more exotic materials such as titanium alloys or MP-35N, were utilized. Although generally performing well in marine environments, the latter materials are usually much more expensive than stainless steels. A need was recognized for less costly materials for use in marine environments which would have greater resistance to crevice corrosion than Type 316. Thus, a new generation of austenitic and ferritic stainless steels was developed, usually employing molybdenum as an alloying element to stabilize the passive film in chloride-containing media and thus reduce susceptibility to crevice corrosion.

---

*A complete list of references appears on page 23.

A number of claims of marine corrosion resistance have been made for these newer stainless steels, some of which have been supported by service experience or laboratory data. The ferric-chloride laboratory test employing either rubber bands or a multiple-crevice washer as the crevice former is usually used to determine crevice corrosion performance. The primary type of test utilized for judging marine crevice corrosion resistance should be an actual marine exposure, and such a test utilizing a multiple-crevice washer, has been described.[3,4] This test, when conducted with certain restrictions, is a good method for comparing the performance of materials in any single test run. Although every effort is made to make both the specimen surface and the crevice washer as flat as possible, some very slight difference of pressure may exist between crevice sites on a panel. This difference in pressure can lead to a slight difference in crevice gap. This can result in a large difference in the time and degree of crevice initiation.[5,6] Minor differences in assembly procedure can affect the crevice gaps, thus changing the number of sites with the critical gap necessary to cause initiation. This makes the comparison of materials from different studies difficult. It was therefore decided for this study that the relative performance of the alloys of interest could best be judged by exposure of all of these alloys, even though data for some of the alloys is available in the literature.

MATERIALS

Thirty-six wrought and nine cast stainless steels and related passive alloys, most containing molybdenum, were selected for this study. Most were selected because of a possibility, based on composition or manufacturers claims, of the material having a greater resistance to crevice corrosion in seawater than Type 316. A few were selected because of an interest in compositional differences. All alloys selected are commercially available. No experimental heats were tested. Tables 1 through 6 list the materials tested and the ladle compositions provided by the manufacturers. Producers of several other alloys were contacted, but materials could not be readily obtained in plate form for tests.

Specimens were prepared in the form of 100- x 150-mm* panels with thicknesses ranging from approximately 0.5 to 5 mm. Each of the panels had ground edges with a stenciled identification number on the face near one edge. A 13-mm-diameter hole was drilled in the center of each panel to allow for the attachment of the crevice formers. All specimens were provided with a common surface finish in the area of the crevice former by grinding a 50-mm-diameter area with wet 120-grit silicon-carbide abrasive papers. In the case of all cast materials and several wrought materials with extremely course as-produced finishes, machining of part or all of the faces was required prior to final surfacing.

TABLE 1 - AUSTENITIC 6% to 16% NICKEL ALLOYS

Alloy	Composition (wt %)							Other			UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S					
T316	17.5	10.7	2.4	1.60	0.04	0.52	0.004	0.03 P	-	0.28 Cu	S31600	-
34LN	16.8	13.76	4.21	1.57	0.03	0.52	0.004	-	0.14 N	-	-	-
T216*	20.	6.	2.5	8.	0.08	1.	-	-	0.35 N	-	S21600	XM-17
Rex 734	21.32	9.44	2.67	3.81	0.04	0.26	0.005	0.30 Nb	0.42 N	0.0025 B	-	-
T317L	18.92	12.25	3.58	1.71	0.025	0.20	0.009	0.035 P	0.056 N	-	S31703	832SNR
317 LM	19.52	14.52	4.08	1.32	0.016	0.40	0.025	0.28 Co	0.056 N	0.16 Cu	-	-
317L+	18.30	15.80	4.25	1.49	0.010	0.63	0.006	0.16 Co	-	0.16 Cu	-	-
22-13-5	21.08	13.70	2.28	4.81	0.045	0.47	0.025	-	-	-	S20910	XM-19, Nitronic 50

*Nominal

*Definitions of abbreviations used are given on page v.

TABLE 2 - AUSTENITIC 17% TO 40% NICKEL ALLOYS

Alloy	Composition (wt %)							Other			UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S					
904L	20.5	24.7	4.7	1.46	0.014	0.46	0.005	-	-	1.57 Cu	-	-
4X	20.15	24.38	4.44	1.45	0.014	0.57	0.001	0.19 P	-	-	-	AL-4X
700	20.70	25.20	4.45	1.65	0.013	0.42	0.008	0.28 Nb	-	0.24 Cu	N08700	Jessup 700
254 SLX	19.9	25.0	4.67	1.64	0.011	0.45	0.003	-	0.042 N	1.67 Cu	N08904	-
777	20.80	25.6	4.48	1.37	0.023	0.48	0.013	0.24 Nb	0.25 Co	2.18 Cu	-	Jessup 777
254 SMO	20.0	17.9	6.1	0.49	0.013	0.41	0.008	-	0.203 N	0.78 Cu	-	-
6X	20.35	24.64	6.45	1.39	0.018	0.41	0.001	-	-	-	-	AL-6X
20 Mod	21.58	25.52	4.95	0.90	<0.01	0.49	-	-	0.49 Co	<0.05 Cu	N08320	Haynes 20 Mod
20 Cb-3	19.36	33.22	2.15	0.44	0.020	0.36	0.002	0.51 Nb	-	3.19 Cu	N08020	-
20 Mo 6	23.91	33.44	5.65	0.44	0.031	0.35	0.007	-	-	3.27 Cu	-	-
254 SFER	29.4	22.2	2.13	1.72	0.016	0.30	0.001	-	0.145 N	0.06 Cu	-	-

TABLE 3 - AUSTENITIC >40% NICKEL ALLOYS

Alloy	Composition (wt %)							Other					UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S							
825	22.02	44.03	2.74	0.35	0.01	0.07	0.004	0.70 Ti		1.66 Cu		Bal Fe	N08825	Incoloy 825
G	22.22	46.84	5.78	1.52	0.007	0.43	-	0.28 W	2.07 Nb	1.85 Cu	1.27 Co	Bal Fe	N06007	Hastelloy G
G-3	22.76	43.69	7.01	0.82	0.006	0.37	-	0.95 W	0.19 Nb	1.85 Cu	3.49 Co	Bal Fe	-	Hastelloy G-3
625	22.29	61.02	8.48	0.10	0.03	0.24	0.001	0.24 Ti	3.57 Nb+Ta	-	-		N06625	Inconel 625
C-276	15.51	54.72	15.49	0.46	0.003	0.04	-	3.82 W	-	0.11 Cu	1.89 Co		N10276	Hastelloy C-276

TABLE 4 - DUPLEX AUSTENITIC-FERRITIC ALLOYS

Alloy	Composition (wt %)							Other			UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S					
T329	26.98	4.22	1.39	0.28	0.052	0.39	0.014	-	-	0.09 Cu	S32900	Carpenter 7-Mo
44LN	25.0	5.9	1.46	1.75	0.028	0.53	0.003	-	0.19 N	0.12 Cu	-	-
Ferralium	26.15	5.64	3.20	0.77	0.02	0.37	-	0.16 Co	0.19 N	1.75 Cu	-	-

TABLE 5 - FERRITIC ALLOYS

Alloy	Composition (wt %)							Other				UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S						
T439	17.66	0.31	0.03	0.26	0.047	0.70	0.010	1.68 Al	-	0.40 Ti	-	S43035	18-SR
T444	18.92	0.07	1.99	0.43	0.020	0.56	0.004	0.020 P	0.012 N	0.13 Ti	0.39 Nb	S44400	17-2
26-1	25.9	0.13	1.00	0.10	0.002	0.29	0.015	0.010 P	0.006 N	-	0.10 Nb	S44627	XM-27, E-Brite 26-1
26-1S	25.05	0.15	0.96	0.17	0.054	0.16	0.011	0.015 P	0.009 N	1.06 Ti	-	S44626	XM-33
29-4	29.6	0.07	4.00	0.10	0.003	0.04	0.011	0.013 P	0.012 N	-	-	S44700	-
29-4C	28.85	0.79	3.81	0.22	0.012	0.19	0.002	-	0.026 N	0.59 Ti	-	-	-
29-4-2	29.5	2.20	3.95	0.10	0.002	0.10	0.010	0.010 P	0.013 N	-	-	S44800	-
SC-1	25.56	2.14	2.94	0.20	0.01	0.25	0.004	0.04 Al	0.016 N	0.51 Ti	-	S44660	SeaCure
Monit	25.3	4.1	3.8	0.43	0.012	0.31	0.006	0.37 Cu	-	-	-	S44635	-

TABLE 6 - CAST ALLOYS

Alloy	Composition (wt %)							Other		UNS No.	Other Common Designations
	Cr	Ni	Mo	Mn	C	Si	S				
CA6N	12.44	8.0	-	0.18	0.02	0.64	0.013	0.010 P	-	-	
CF8M	19.30	10.05	2.36	0.95	0.04	0.79	0.019	-	-	J92900	Cast T316, ESCO 33 G
IN 862	20.92	24.46	5.00	0.47	0.03	0.52	0.009	0.007 P	-	-	-
CN7MS	19.37	22.10	2.93	1.00	0.05	3.00	0.010	0.006 P	1.55 Cu	J94650	Worthite
CN7M	20.01	28.18	2.51	0.18	0.04	0.76	0.025	0.007 P	3.12 Cu	J95150	Alloy 20, ISA 20
625	20.58	63.7	8.53	0.02	0.02	0.01	0.011	0.006 P	3.48 Nb	-	-
CW 12M-2	18.10	62.8	17.58	0.54	0.01	0.56	0.007	0.010 P	0.08 Cu	-	Illium W-2, Chlorimet 3
Illium PD	24.55	5.39	1.97	0.86	0.04	0.80	0.016	0.004 P	5.74 Co	-	-
Ferralium*	25.2	5.2	2.5	1.	-	1.10	-	-	3.2 Cu	-	-

*Nominal

EXPERIMENTAL PROCEDURE

Specimens were first degreased in acetone, then pumice-scrubbed with a bristle brush, rinsed with water, rinsed with fresh acetone, and finally dried. Crevice formers consisting of grooved Delrin washers were then secured to both sides of each test panel with an insulated titanium fastener. Each washer had 20 plateaus in contact with the plate and each had been previously ground to a 600-grit finish using silicon-carbide paper before assembly. A torque wrench was used to supply a torque of 8.5 N·m to the bolts, and lack of electrical continuity between the bolt and the panel was verified with an ohmeter. The final assembly had a boldly exposed-surface/shielded-surface area ratio of 150:1.

The completed assembly, as illustrated in Figure 1, was then mounted on a plastic rack using the titanium fastener to avoid creation of additional crevices, and the racks placed in the seawater test apparatus.

All materials were tested in triplicate. Exposure duration was 30 days. All wrought materials were exposed simultaneously in the same run, and all cast materials were exposed simultaneously in a second run. To minimize run-to-run variations, panels for both runs were exposed using the same apparatus and procedures, within 4 months of each other. Precautions were taken to minimize the variability between the wrought and the cast material runs.

Specimens were inspected during the course of the test for visual signs of accumulated corrosion product. Observations were made without disturbing or removing the specimens from the seawater. Inspections were conducted on an almost daily basis with an increased frequency during the first week of exposure. The observations provided some indication of approximate times to initiation of crevice corrosion; however, the actual times to initiation could differ from those determined during the routine inspection, since some finite amount of corrosion might have occurred prior to the buildup of corrosion products.

Upon completion of the scheduled test period and removal of the crevice assemblies, specimens were immersed in cold 30% HNO_3 for 15 minutes, rinsed, and brushed with a pumice-detergent mixture to remove any corrosion products and staining.

Depths of attack at individual crevice sites were measured with a needle-point dial gage to the nearest 0.01 mm. The values reported herein reflect the deepest areas of attack as determined by this method. In several instances, perforations resulting from attack on opposite sides of the specimens were noted. In this case, the depth of attack is considered to be one-half of the material thickness.

Tests were conducted in a controlled temperature ($30^{o}C$) seawater trough equipped with facilities for recirculation and refreshment. Two interconnected, 400-ℓ capacity troughs were utilized for these and concurrent tests. Figure 2 shows a sketch of the apparatus and relative positioning of the crevice specimens. The nominal velocity through the test section was 0.02 m/sec. Fresh, filtered seawater was introduced at a rate which provided approximately six to seven complete changes daily.

EXPOSURE RESULTS

AUSTENITIC WITH 6% TO 16% NICKEL

Exposure results for austenitic alloys containing 6% to 16% nickel are presented in the top of Table 7. All alloys suffered attack on at least one crevice site on all sides of the triplicate panels. Three materials, 34LN, 317LM, and 22-13-5 showed at least 12 sites attacked per side; whereas, the other alloys had at least one side with fewer than eight sites attacked. The variability in the number of sites attacked was too large to make clear distinctions in material behavior, however. For alloys with less than 2% manganese, low molybdenum and nickel concentrations corresponded with higher maximum depths of attack, although this correspondence is not clear cut. Any other effects on crevice corrosion of nickel additions from 6% to 16%, of manganese additions up to 8%, or of chromium additions from 12% to 21% were not statistically significant. Ranges of initiation times were generally small, with most sites on these materials initiating in approximately 50 to 100 hr (2 to 4 days). The number of sites attacked and the initiation time were not influenced by molybdenum additions up to 4.25%. Several specimens experienced gravity-related attack, as illustrated in Figure 3. Gravity-related attack initiates either at crevice sites or panel edges and always proceeds by tunneling downward. This attack may be due to an effect of corrosion products lying on the bottom of the attacked area, creating an additional crevice site. Type 317L experienced tunneling initiating at the crevice sites and proceeding downward.

TABLE 7 - CREVICE CORROSION RESULTS FOR AUSTENITIC ALLOYS

Material	Approximate Composition (wt %)					No. of Sites Attacked		No. of Sides Attacked	Depth of Attack (mm)	Initiation Time (hr)
	Cr	Ni	Mo	Mn	Cu	Per Side	Total			
T316	17.5	10.7	2.4	1.6	0.3	1-13	33	6	0.29-1.93	24-102
34 LN	16.8	13.8	4.2	1.6	-	12-20	102	6	0.10-1.04*	36-102
T216	20.	6.	2.5	8.	-	7-10	50	6	0.10-0.64	51-77
Rex 734	21.3	9.4	2.7	3.8	-	2-9	39	6	0.01-1.00	51
T317L	18.9	12.2	3.6	1.7	-	7-20	91	6**	0.18-1.92	51-77
317LM	19.5	14.5	4.1	1.3	0.2	19-20	116	6	0.01-1.07	51-77
317L+	18.3	15.8	4.2	1.5	0.2	1-12	44	6***	0.18-1.09	51-479
22-13-5	21.1	13.7	2.3	4.8	-	16-20	112	6	0.10-1.10	36-77
904L	20.5	24.7	4.7	1.5	1.6	0-13	36	5	0.14-0.74	51-365
4X	20.2	24.4	4.4	1.4	-	0-4	8	4	0.14-0.50	77-245
700	20.7	25.2	4.4	1.6	0.2	0-20	47	5	0.08-2.00	51-171
254 SLX	19.9	25.0	4.7	1.6	1.7	7-15	70	6	0.08-0.92	51-77
777	20.8	25.6	4.5	1.4	2.2	8-12	60	6	0.03-2.90	36-77
254 SMO	20.0	17.9	6.1	0.5	0.8	0-7	18	5	0.02-0.51	51-479
6X	20.4	24.6	6.4	1.4	-	0-3	11	4	0.01-0.62	51-365
20 Mod	21.6	25.5	5.0	0.9	-	0-5	6	2	0.12-0.46	51-365
20 Cb-3	19.4	33.2	2.2	0.4	3.2	0-15	49	5	0.14-3.10	51-171
20 Mo-6	23.9	33.4	5.6	0.4	3.3	0-6	13	3	<0.01-0.53	365-507
254 SFER	29.4	22.2	2.1	1.7	0.1	0-3	11	5	0.34-0.90	102-221
825	22.0	44.0	2.7	0.4	1.7	4-13	37	6**	0.25-2.42	51-221
G	22.2	46.8	5.8	1.5	1.8	0-2	6	4	0.02-0.87	365-673†
G-3	22.8	43.7	7.0	0.8	1.8	0-2	2	1	0.06-0.21	102
625	22.3	61.0	8.5	0.1	-	0	0	0	-	-
C-276	15.5	54.7	15.5	0.5	0.1	0	0	0	-	-

*Specimen perforated.
**Gravity-assisted tunneling.
***Some attack initiating outside of crevice area.
†Initiation not observed on some panels where attack occurred.

AUSTENITIC WITH 17% to 40% NICKEL

Exposure results for the austenitic alloys containing 17% to 40% nickel are presented in the middle of Table 7. These alloys tended to experience a wider range in the number of sites attacked, depth of attack, and initiation time than the lower nickel alloys. In addition, for all of the materials except 254SLX and 777, at least one side of one panel was unattacked. Materials 254SLX and 777 had the largest total number of sites attacked and were the only materials in this group experiencing attack on all six specimen sides. Although not totally conclusive, there was a trend for materials highest in molybdenum to have the lowest depths of attack, while those low in molybdenum had the greatest depths of attack. This could be due to a longer initiation time in the higher molybdenum alloys resulting in a shorter time available for propagation. The amount of other elements in the alloy - chromium, nickel, manganese, and copper - had a statistically insignificant effect on the crevice corrosion behavior of the materials.

AUSTENITIC WITH >40% NICKEL

Exposure results for the nickel-base materials, those with greater than 40% nickel, are presented in the bottom of Table 7. Behavior of these materials was a strong function of molybdenum content. Alloy 825 behaved similarly to the lower nickel materials of similar molybdenum concentration and even experienced gravity-related tunneling attack. The performance of the alloys improved with increasing molybdenum content. Alloys with greater than 8% molybdenum were unattacked in this exposure. Any effects of varying compositions of chromium, nickel, or manganese were completely overridden by the molybdenum effect.

DUPLEX AUSTENITIC-FERRITIC

Exposure results for the duplex alloys with 4% to 6% nickel and consisting of a microstructure containing both austenite and ferrite are presented in the top of Table 8. Once again, data variability is quite high but, even so, the beneficial effect of molybdenum is still quite obvious, while the effect of the other elements is insignificant by comparison.

TABLE 8 - CREVICE CORROSION RESULTS FOR DUPLEX AND FERRITIC ALLOYS

Material	Approximate Composition (wt %)					No. of Sites Attacked		No. of Sites Attacked	Depth of Attack (mm)	Initiation Time (hr)
	Cr	Ni	Mo	Mn	Cu	Per Side	Total			
T329	27.0	4.2	1.4	0.3	0.1	9-15	73	6	0.02-1.29*	51-102
44LN	25.0	5.9	1.5	1.8	0.1	14-20	104	6	0.04-3.35	36-51
Ferralium	26.2	5.6	3.2	0.8	1.8	0-1	2	2	0.03-0.08	365†
T439	17.7	0.3	-	0.3	-	1-17	58	6**	0.42-0.72*	24-77
T444	18.9	0.1	2.0	0.4	-	6-12	54	6	0.33-1.21*	51-245
26-1	25.9	0.1	1.0	-	-	0-5	10	4	0.15-0.46	51-107
26-1S	25.0	0.2	1.0	0.2	-	0-2	6	4	0.06-0.30	171-553
29-4	29.6	0.1	4.0	-	-	0	0	0	-	-
29-4C	28.8	0.8	3.8	0.2	-	0	0	0	-	-
29-4-2	29.5	2.2	4.0	-	-	0	0	0	-	-
SC-1	25.6	2.1	2.9	0.2	-	0-1	1	1	0.05	†
Monit	25.3	4.1	3.8	0.4	0.4	0	0	0	-	-

*Specimen perforated.
**Gravity-assisted tunneling; some attack initiating outside of crevice area.
†Initiation not observed on some panels where attack occurred.

FERRITIC

Exposure results for the ferritic alloys containing less than 2.5% nickel are presented in the bottom of Table 8. Once again the molybdenum effect is dramatic. Type 439 with no molybdenum experienced such extensive gravity-related tunneling that one panel was nearly divided in half. Chromium levels of 25% were necessary for the beneficial effect of 1% to 2% molybdenum to be seen. The molybdenum level necessary to completely prevent attack in these alloys appears, within the limits of the data variability, to be around 3.5%. SC-1 with 2.9% molybdenum experienced attack on only one site, while the 3.8% to 4.0% molybdenum alloys experienced no attack. Thus going from an austenitic to a totally ferritic structure reduced the molybdenum required to prevent attack from about 8% to around 3.5%.

CAST ALLOYS

Exposure results for the cast alloys are presented in Table 9. Molybdenum had a beneficial effect on both the number of sites attacked and on the depths of attack. Cast Ferralium performed significantly worse than its wrought counterpart, although this could be due to the nearly 1% lower molybdenum content in the casting. CA6N, CN7MS, and CN7M all experienced a consistantly large number of sites attacked on all sides, Alloy 625 and CW 12M-2 with more than 8% molybdenum experienced no attack, and the remainder of the materials displayed a large variability in the number of sites attacked. Although initiation was not detected in many cases, the observed initiation times of most sites on these materials ranged from approximately 125 to 175 hr (5 to 7 days).

TABLE 9 - CREVICE CORROSION RESULTS FOR CAST ALLOYS

Material	Approximate Composition (wt %)					No. of Sites Attacked		No. of Sites Attacked	Depth of Attack (mm)	Initiation Time (hr)
	Cr	Ni	Mo	Mn	Cu	Per Side	Total			
CA6N	12.4	8.0	-	0.2	-	15-20	111	6**,***	0.01-2.00	126-169+
CF8M	19.3	10.0	2.4	1.0	-	4-17	74	6	0.16-3.77	126+
IN-862	20.9	24.5	5.0	0.5	-	1-16	52	6	0.12-1.22	126-217+
CN7MS	19.4	22.1	2.9	1.0	1.6	14-20	102	6***	0.08-3.82	126
CN7M	20.0	28.2	2.5	0.2	3.1	13-18	99	6**,***	0.15-2.33	126+
625	20.6	63.7	8.5	-	-	0	0	0	-	-
CW 12M-2	18.1	62.8	17.6	0.5	0.1	0	0	0	-	-
Illium PD	24.6	5.4	2.0	0.9	-	3-20	73	6	0.08-4.53	48-126+
Ferralium	25.2	5.2	2.5	1.0	3.2	0-14	37	4***	0.03-2.21	126-169

** Gravity-assisted tunneling.
*** Some attack initiating outside of crevice area.
+ Initiation not observed on some panels where attack occurred.

COMPARISON WITH PREVIOUS STUDIES

These results are in general agreement with a number of more limited studies[4,5,7-19] with a few minor exceptions. The severity of attack was generally greater in this study than in the previous work. This investigation employed surface-grinding of the specimen faces, plastic crevice washers torqued to relatively high levels of 8.5 N·m, a very unfavorable crevice/bold area ratio, and controlled-temperature, filtered, natural seawater. Many previous investigations employed as-produced surfaces, lower or undefined torque levels, ambient temperature seawater, or artificial seawater in their studies. In some cases, biofouling may have covered portions of the boldly exposed surfaces. Some of these conditions could lead to less aggressive attack than in the present study.[5,9] For example, 254SMO and 6X both experienced light attack in this study and one similar study,[20] even though many previous investigators have been unable to initiate attack on these materials for periods of up to 2 years.[7-11] Also, both initiation and propagation rates of the austenitic alloys with 6% to 16% nickel tends to be worse than that previously reported in some instances. This only confirms the necessity for the testing of all alloys under consistant conditions in order to be able to make viable performance comparisons.

EFFECTS OF ALLOYING ADDITIONS

The beneficial effect of molybdenum, and to a lesser extent chromium, on crevice corrosion resistance has been documented.[8-10,21-24] The beneficial effect of molybdenum was also apparent in this study, with complete freedom from attack being experienced by austenitic alloys with 8% molybdenum and ferritic alloys with about 3.5% molybdenum. This is similar to the results of other investigators who determined these values to be 6% for austenitics and 3% for the ferritics.[8,9] As noted in other investigations,[8,9] ferritic alloys with less than 25% chromium did not, in this study, experience the beneficial effects of 1% to 2% molybdenum. Otherwise the effect of chromium on crevice corrosion behavior was insignificant compared to the data scatter. Nickel content also had little effect on the crevice corrosion performance except as related to change in structure. Other alloying elements also had statistically insignificant effects on crevice corrosion behavior in this study.

RELATIVE PERFORMANCE OF ALLOYS

Data variability in this study is large, therefore a detailed ranking of materials is not possible. Materials can be placed in groups, however, as long as it is recognized that the test variability could lead to an occasional material being placed in the wrong group. Table 10 presents such a grouping, based on the minimum number of sites attacked per side. It is recognized that in some applications the depth of attack may be the more important consideration, and this would affect the grouping. This grouping is not meant to suggest that all materials within a group will behave similarly in service, only that their behavior could not be separated with any confidence in this study. For example, it is likely that the extra 2% molybdenum in 6X compared to the 4X material will enable the 6X to perform satisfactorily over a larger range of crevice geometries than 4X. The placement of these alloys in the same group indicates only that for the particular crevice geometry in this study, the behavior of the two alloys was similar.

The data presented in this study cannot be extrapolated to service applications unless the differences in crevice geometry and environment between the service application and this study can be proven to be minimal. Even the relative performance of the materials can change as these factors are varied.

INTERPRETATION AND USE OF RESULTS

The variability in both the number of sites attacked and the depth of attack on any one material is likely due to the difficulty in obtaining a reproducible crevice geometry, and in particular, crevice gap. Kain[5] has suggested that extremely small variations in crevice gap can greatly affect the agressiveness of the solution formed in the crevice which leads to passive film breakdown. A "loose" crevice with a large gap, as might be found in a metal-to-metal contact situation on rough surfaces, may give rise to an extremely nonaggressive crevice solution which will not cause initiation of crevice corrosion even on materials which performed poorly in this study. Thus, it is noted that many of the materials which were attacked in this study have performed adequately in service for many years.[1,2,25] Similarly, a "tight" crevice with a small gap, such as the highly torqued plastic-to-metal, ground-surface crevice used in this study, can lead rapidly to an extremely aggressive crevice solution which will cause initiation on even highly resistant materials. For this reason, this multiple-crevice assembly exposure is considered as a highly severe crevice corrosion test, and materials should not be ruled out in a service application strictly because they experienced attack in this study.

TABLE 10 - RELATIVE PERFORMANCE OF ALLOYS IN MULTIPLE-CREVICE TEST

No Attack (0 sites/side)	Minimal Attack (0 to 7 sites/side)	Variable Attack (0 to 20 sites/side)	Heavy Attack (at least 12 sites/side, minimum)
625	4X	T316	34LN
C-276	254 SMO	T216	317LM
29-4	20 Mod	Rex 734	22-13-5
29-4C	20 Mo-6	T317L	44LN
29-4-2	254 SFER	317L+	CA6N Cast
Monit	G	904L	CN7MS Cast
625	G-3	700	CN7M Cast
CW 12M-2 Cast	Ferralium	254 SLX	
	26-1S	777	
	SC-1	20 Cb-3	
		825	
		T329	
		T439	
		T444	
		CF 8M Cast	
		IN-862 Cast	
		Illium PD Cast	
		Ferralium Cast	

Since the crevice severity in any service environment cannot be easily quantified, alloy selection must be based on service experience with comparable types of crevices. Generally, if a material performs well in service, any material performing better in this study is likely to also perform well in the same service application. Similarly, a material performing poorly in service should not be replaced with one performing even worse in this study. In a borderline situation, where the service performance of a material is marginal, the use of a material performing significantly better in this study may lead to satisfactory service performance.

Caution should be applied when judging the relative performance of materials from this study. The multiple-crevice assembly may have a range of crevice gaps which would account for the large amount of data scatter.[5,6] Small differences in performance are therefore not significant. For example, 254 SMO had 18 total sites attacked with up to seven sites attacked on a single side of a panel, while 6X had only 11 total sites attacked with only up to three sites on a panel side. Yet other investigators have been unable to get crevice attack on either material,[7,11,18] and both perform equivalently well in service. Thus, small differences in behavior seen in this study are mainly a result of statistical variability in the data.

CONCLUSIONS

There presently exist a number of commercially available austenitic and ferritic stainless steel alloys which are more resistant to crevice corrosion in seawater than Type 316. Several of these alloys displayed resistances to crevice corrosion in this study equivalent to the highly resistant and more costly nickel-base alloys.

The austenitic alloys studied required 8% molybdenum to prevent crevice corrosion in these exposures, while the ferritic alloys required 25% chromium and about 3.5% molybdenum to prevent localized attack. The effect of other alloying elements on localized corrosion in this study was insignificant compared to the data scatter.

The behavior of the alloys has been grouped as follows: no attack, minimal attack, variable attack and heavy attack. Caution must be observed, however, in using this grouping to predict service performance.

ACKNOWLEDGMENTS

The author wishes to acknowledge the extensive contributions of Mr. R. M. Kain of the LaQue Center for Corrosion Technology in the design and conduct of this investigation. The author also wishes to acknowledge Mr. T. S. Lee of the LaQue Center for Corrosion Technology who, along with Mr. Kain, helped to gather together the materials for testing. Material for test was provided without charge by Allegheny Ludlum, Armco, Avesta Jernverks, Cabot, Carpenter Technology, Crucible, Eastern, Firth-Brown, Huntington, Jessup, Langley Alloys, and Uddeholm.

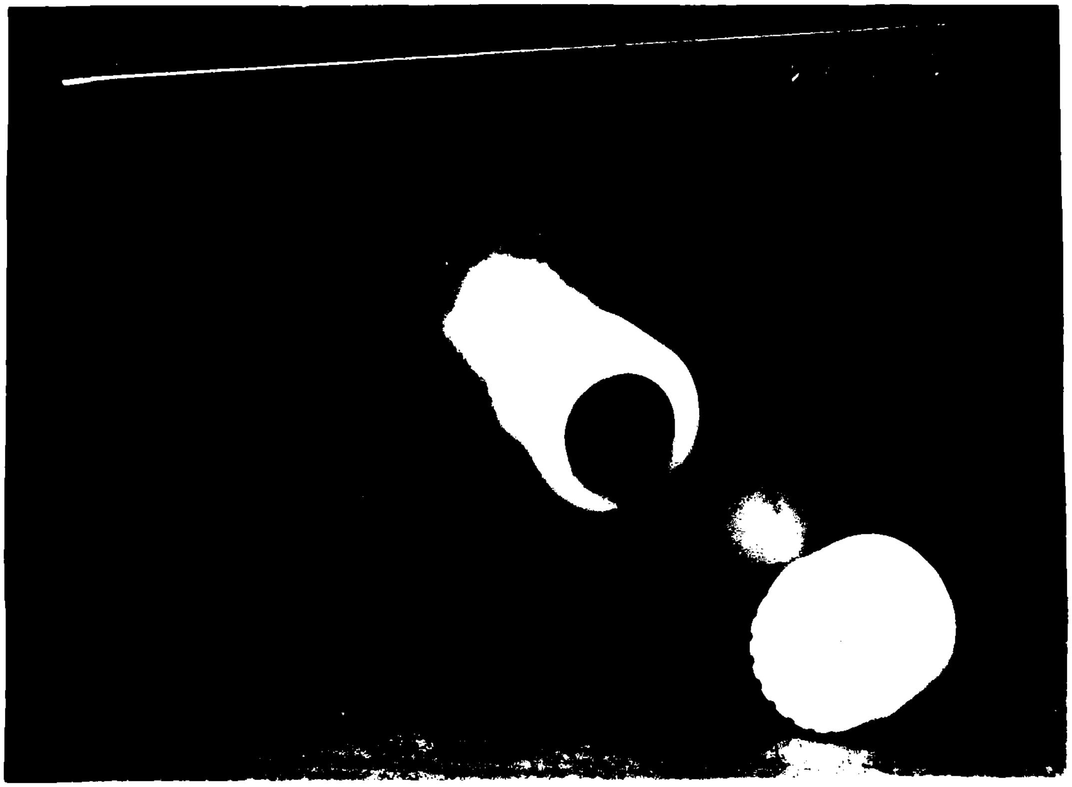


Figure 1 - Multiple Crevice Assembly

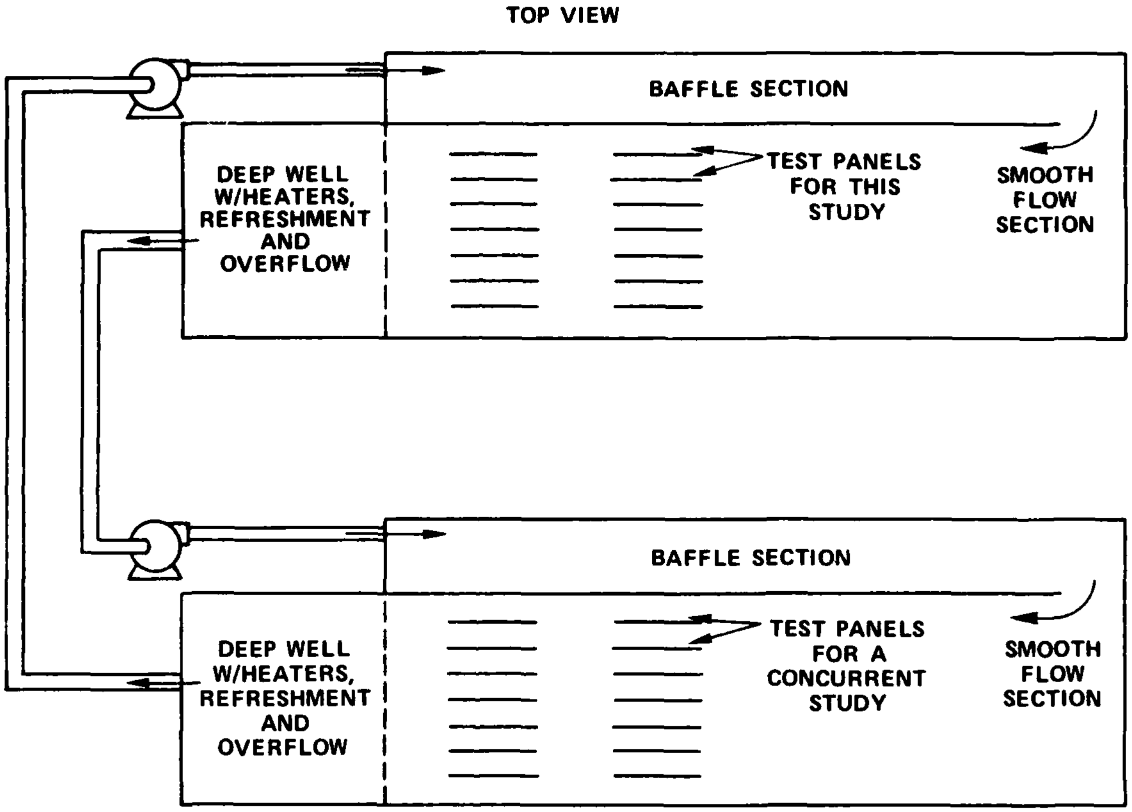


Figure 2 - Exposure Troughs

317

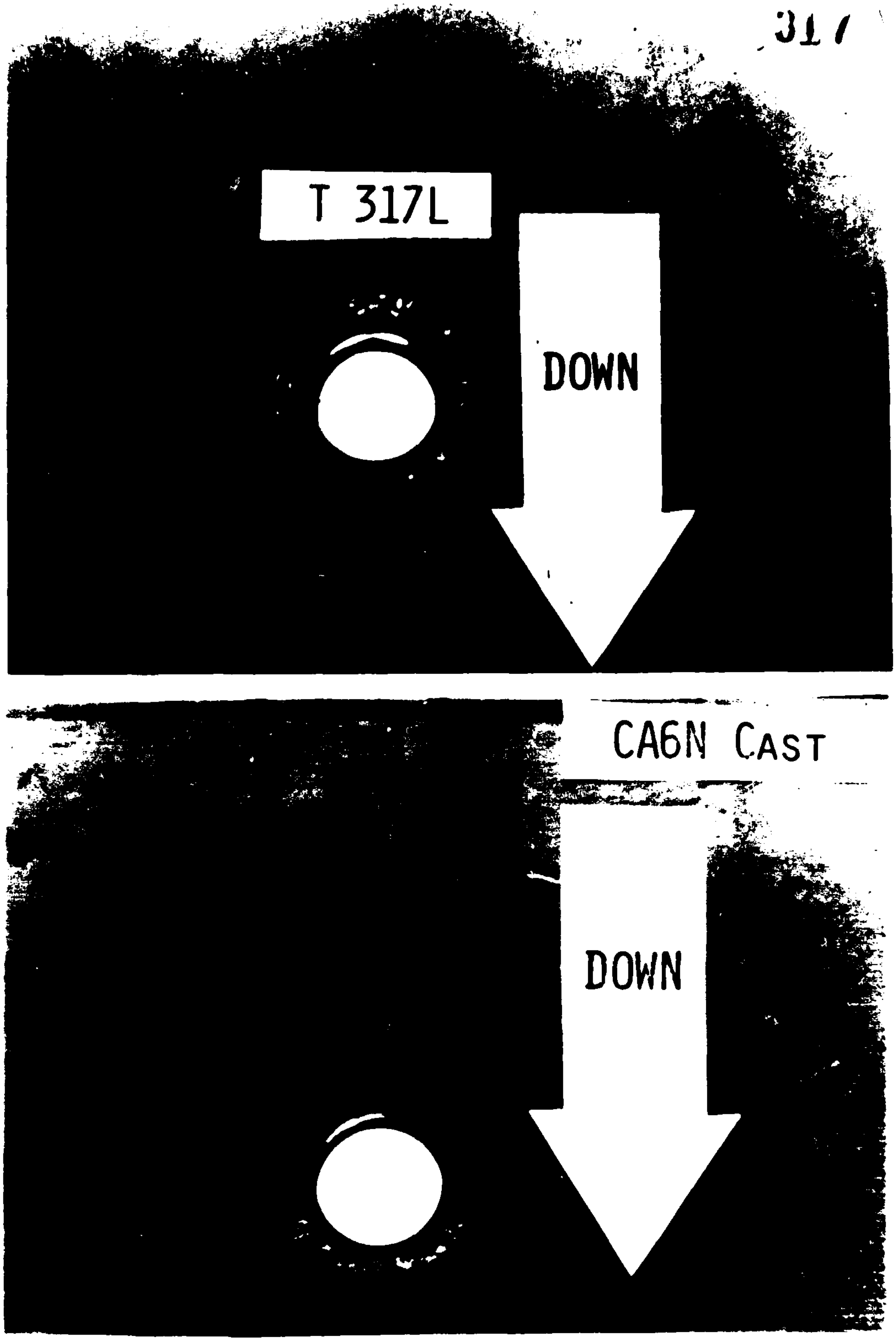


Figure 3 - Gravity-Induced Tunneling

REFERENCES

1. Deverall, H. E., and J. R. Maurer, "Stainless Steels in Seawater," Materials Performance, Vol. 17, No. 3 (Mar 1978).

2. Harada, K., T. Suzuki, and K. Ishii, "Applications of 18Cr-2Mo Ferritic and High Chromium Ferritic/Austenitic Stainless Steels in Japan," Paper 13 presented at Stainless Steel '77, London, England (Sep 1977).

3. Anderson, D. B., "Statistical Aspects of Crevice Corrosion in Seawater," Galvanic and Pitting Corrosion, ASTM STP 576 (1976).

4. Kain, R. M., "Localized Corrosion Behavior in Natural Seawater; A Comparison of Electrochemical and Crevice Testing of Stainless Alloys," Paper 74 presented at Corrosion/80, Chicago, IL (May 1980).

5. Kain, R. M., "Crevice Corrosion of Stainless Steels in Seawater and Related Environments," Paper 200 presented at Corrosion/81, Toronto, Canada (Apr 1981).

6. Kain, R. M., "Crevice Corrosion and Metal Ion Concentration Cell Corrosion Resistance of Candidate Materials for OTEC Heat Exchangers, Parts I and II," U.S. Department of Energy, Report ANL/OTEC-BCM-022.

7. Wallen, B., and M. Liljas, "Avesta 254 SMO - A New, High Molybdenum Stainless Steel," presented at NKM8, Helsinki (Aug 1978).

8. Redmond, J. D., "Corrosion Resistance of Stainless Steels in Seawater," Supplement Report RP-33-77-14, Climax Molybdenum, Pittsburgh, PA (1977).

9. Bond, A. P., and H. J. Dundas, "Corrosion Resistance of Stainless Steels in Seawater," Report RP-33-79-10, Climax Molybdenum, Ann Arbor, MI (Nov 1980).

10. Bond, A. P., et al, "Stainless Steels for Seawater Service," Paper 15 presented at Stainless Steel '77, London, England (Sep 1977).

11. Wallen, B., "Avesta 254 SMO - A Stainless Steel for Seawater Service," presented at the Advanced Stainless Steels for Turbine Condensors Operating in Seawater Seminar sponsored by Associazione Italiana di Metallurgia, Piacenta (1980).

12. "Ferralium Alloy - A New High Strength Super Stainless Steel, Preliminary Data," Bulletin F-30, 488B, Stellite Division, Cabot Corp., Kokomo, IN.

13. Streicher, M. A., "Microstructures and Some Properties of Fe-28% Cr-4% Mo Alloys," Corrosion, Vol. 30, No. 4 (Apr 1974).

14. Lennox, T. J., Jr., and M. H. Peterson, "Corrosion Resistance and Cathodic Protection of Recently Developed Stainless Steel Alloys in Seawater," Materials Performance, Vol. 15, No. 6 (Jun 1976).

15. Garner, A., "Crevice Corrosion of Stainless Steels in Seawater - Correlation of Field Data with Laboratory Ferric Chloride Tests," Corrosion, Vol. 37, No. 3 (Mar 1981).

16. Krougman, J. M., and F. P. IJsseling, "Crevice Corrosion of Stainless Steels and Nickel Alloys in Seawater," Report 1977-45, Koninklijh Institut Voor De Marine Corrosielaboratorium (Nov 1977).

17. Asphahani, A. I., "Corrosion Resistance of High Performance Alloys," Materials Performance, Vol. 19, No. 12 (Dec 1980).

18. Kovach, C. W., and L. S. Redmerski, "Crevice Corrosion of Type 316 and Highly Alloyed Stainless Steels in Simulated Natural Environments Using the Multiple Crevice Assembly," Paper 123 presented at Corrosion/81, Toronto, Canada (Apr 1980).

19. Krougman, J. M., and F. P. IJsseling, "Crevice Corrosion of Austenitic Stainless Steel X3 CrNiMoN 17 13 5 in Seawater," Report 1975-29, Koninklijk Institut Voor De Marine Corrosielaboratorium (Dec 1975).

20. Kain, R. M., "Crevice Corrosion Resistance of Several Iron and Nickel Base Cast Alloys in Seawater," Paper 66 presented at Corrosion/82, Houston, T (Mar 1982).

21. Tomashov, N. D., et al, "Effect of Supplementary Alloying Elements on Pitting Corrosion Susceptibility of 18Cr-14Ni Stainless Steel," Corrosion, Vol. 20, No. 5 (May 1964).

22. Steigerwald, R. F., et al, "The New Fe-Cr-Mo Ferritic Stainless Steels," Corrosion, Vol. 33, No. 8 (Aug 1977).

23. Bond, A. P., "Corrosion of High-Purity Ferritic Stainless Steels in Various Environments," Report RP-33-1969-1, Climax Molybdenum, Ann Arbor, MI (May 1970).

24. "Corrosion and Polarization Behavior of High Purity Ferritic Stainless Steels," Report RP-33-69-09, Climax Molybdenum, Ann Arbor, MI (Feb 1971).

25. Nichol, T. J., et al, "Applications of New High Chromium Ferritic Stainless Steels in the Chemical Process Industries," Paper 117 presented at Corrosion/81, Toronto, Canada (Apr 1981).

INITIAL DISTRIBUTION

Copies	
7	NAVSEA
	1 SEA 05
	2 SEA 05R15
	2 SEA 05E1
	2 SEA 99612
2	NTIC
2	DTIC

CENTER DISTRIBUTION

Copies	Code	
1	28	(Belt)
3	2803	
1	2809H	(Hudak)
10	281	(Wacker)
10	2813	(Morton)
25	2813	(Hack)
2	2814	(Gudas)
1	282	(Crisci)
1	522.1	(Unclass. Library)
2	5231	(Office Services)

DTNSRDC ISSUES THREE TYPES OF REPORTS

1. DTNSRDC REPORTS, A FORMAL SERIES, CONTAIN INFORMATION OF PERMANENT TECHNICAL VALUE. THEY CARRY A CONSECUTIVE NUMERICAL IDENTIFICATION REGARDLESS OF THEIR CLASSIFICATION OR THE ORIGINATING DEPARTMENT.

2. DEPARTMENTAL REPORTS, A SEMIFORMAL SERIES, CONTAIN INFORMATION OF A PRELIMINARY, TEMPORARY, OR PROPRIETARY NATURE OR OF LIMITED INTEREST OR SIGNIFICANCE. THEY CARRY A DEPARTMENTAL ALPHANUMERICAL IDENTIFICATION.

3. TECHNICAL MEMORANDA, AN INFORMAL SERIES, CONTAIN TECHNICAL DOCUMENTATION OF LIMITED USE AND INTEREST. THEY ARE PRIMARILY WORKING PAPERS INTENDED FOR INTERNAL USE. THEY CARRY AN IDENTIFYING NUMBER WHICH INDICATES THEIR TYPE AND THE NUMERICAL CODE OF THE ORIGINATING DEPARTMENT. ANY DISTRIBUTION OUTSIDE DTNSRDC MUST BE APPROVED BY THE HEAD OF THE ORIGINATING DEPARTMENT ON A CASE-BY-CASE BASIS.

FILMED

2-8